STANFORD UNIVERSITY LIBRARY

The Volumetric Determination *of* Arsenic Acid

Dissertation

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science of
Columbia University

BY

ROCCO FANELLI, B. S., A. M.

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

NEW YORK CITY
1923

3781
C72F
CLASSED
Dissertation

The Volumetric Determination *of* Arsenic Acid

Dissertation

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science of
Columbia University

BY

ROCCO FANELLI, B. S., A. M.

NEW YORK CITY
1923

ACKNOWLEDGMENT.

This investigation was suggested by Professor H. A. Fales and was carried out under his direction. To him is due my thanks for his kindness and advice received throughout this work.

Of the methods for the quantitative determination of pentavalent arsenic, that of Williamson[1], lends itself most readily, at least in theory, to its estimation. The method consists essentially in the addition of potassium iodide to a strongly acidified arsenate solution and the subsequent titration of the liberated iodine by means of thiosulphate. The reaction is usually written $As_2O_5 + 4HI = As_2O_3 + 2I_2 + 2H_2O$. Although simple in detail, the method has gradually disappeared from standard works on quantitative analysis and more cumbersome and time consuming methods have taken its place. At the time, the method was proposed simply for control work, but this fact has seemingly been overlooked and much has been expected of it in the way of accuracy. On account of the high results and general untruthworthiness of the method, it has been practically abandoned without a thorough investigation of the errors involved.

In view of the simplicity of the method and the fact that in a great many cases arsenic is obtained in a form ready for estimation only after treatment with strong oxidizing agents or fusion mixtures, it was thought advisable to determine the errors in the method and to try to adjust conditions so that reliable results could be obtained.

Historical. Williamson's method first appeared in 1896. Soon after it, Gooch and Morris[2], published a paper pointing out two grave sources of error, namely, the excess liberation of iodine from an acidified potassium iodide solution and the decomposition of thiosulphate when titrating strongly acid solutions of iodine.

They also ran determinations according to the procedure given by Williamson and have shown the method to give results in some cases too high by about 22 parts in a thousand. They recommend an arbitrary correction of .0030 gms. of arsenic acid to be deducted from the indication given by Williamson's process. No attempt was made to reduce the errors to a minimum or to put the method upon a more reliable basis.

In 1906, Rosenthaler[3] published a paper showing that a slight change in procedure gave much better results than those published by Gooch and Morris. Here, again, no attempt was made to fix the magnitude of errors.

In 1919, Kolthoff[4] attempted to fix the acid and potassium iodide concentrations in order to reduce the error due to excess liberation of iodine.

Fleury[5], in 1920, criticized Rosenthaler's procedure and recommended heating the reaction mixture on a water bath with a small amount of

acid in the presence of much potassium iodide. Shortly after the appearance of this paper, Rosenthaler[6] published a series of results in answer to Fleury's criticisms.

In no paper except that of Gooch and Morris was any attempt made to determine the magnitude of errors involved in the method.

The main sources of error may be listed as follows:

(1) The use of starch as an indicator to determine the disappearance of the last traces of iodine.

(2) The liberation of iodine from an acidified potassium iodide solution due to the action of air.

(3) The decomposition of thiosulphate by strong acids.

(4) The concentration of acid in order to secure complete or nearly complete action.

(5) The reversibility of the reaction due to dilution during titration.

I. THE USE OF STARCH AS AN INDICATOR.

In spite of the fact that attention has been called to the lack of sensitiveness of starch in strongly acid solutions as an indicator for iodine, its use is still recommended in some texts and private procedures. While starch will indicate the presence of iodine in acid solutions, the disappearance of the characteristic blue color by titrating with thiosulphate is never sharp but gives a succession of colors which may be due to the presence of dextrins, either present originally in the starch or formed by hydrolysis in the acid solution. For the solutions under consideration this lack of sharpness is due in all probability mainly to the presence of a high concentration of electrolyte.[20] This difficulty in the end point has been observed with different starches and is not characteristic of any particular kind of starch. The gradual change in color from blue to colorless makes it difficult to determine the end point and usually involves a large error due to overtitration.

It is preferable, wherever possible, to employ one of the reacting constituents as an indicator rather than add extraneous material. The color of iodine solutions, especially in small volume, is very distinct, and its disappearance when titrating with thiosulphate solution is surprisingly sharp and easily determined. No difficulty was experienced in determining the disappearance of the iodine color, even in very dilute solutions. After the disappearance of the yellow color, the addition of starch solution shows that no iodine remains and that the disappearance

of color is effective in showing its absence. Its use is strongly recommended in preference to the disappearance of the starch iodide color.

The overtitration with starch as an indicator can easily be shown by titrating an acid solution of iodine, using starch as an indicator, and a similar solution with iodine acting as its own indicator.

II. THE LIBERATION OF IODINE FROM AN ACID SOLUTION OF POTASSIUM IODIDE BY THE ACTION OF AIR.

The liberation of a small amount of iodine upon acidifying potassium iodide solution has been attributed to many things. Iodate, iron and copper[7] in the potassium iodide, the action of light, chlorine in the hydrochloric acid and oxygen dissolved in the solution have all been responsible, more or less, for this liberation of iodine. In general, however, when iodate, iron, copper and chlorine are absent, the liberation of iodine is due, mainly, to the dissolved oxygen in the solution. This can easily be shown by passing oxygen-free nitrogen through an acid solution at room temperature for a period of time to remove dissolved oxygen, and then adding potassium iodide solution. The first tint of iodine becomes apparent only after the lapse of thirty minutes. The addition of potassium iodide to the same strength of acid without the above treatment shows iodine almost instantaneously. Further, an acid solution saturated with oxygen gas liberates more iodine in a given period of time than an acid solution containing air for the same period of time.

The liberation of iodine, although slight, takes place even in neutral solution in the presence of oxygen. This reaction is especially catalyzed by light. The equation for the action may be expressed simply as follows: $4I^- + O_2 + 2H_2O = 2I_2 + 4OH^-$. If the equation is an expression of the facts, then the increase of H^+ would result in a greater increase of liberated iodine, since the removal of OH^- displaces the equilibrium to the right.

Experiment shows that hydriodic acid is very sensitive to oxidation by exposure to air and, in the Williamson method, has proven a serious source of error. This fact was long recognized. Kolthoff tried to avoid this oxidation by carrying out determinations in vacuo, but found that the difference in results obtained was negligible. Rosenthaler[6] tried to displace air from the acid solutions by adding sodium bicarbonate and also by passing carbon dioxide through the solutions. The results appear to be no better than those obtained without the use of sodium bicarbonate and carbon dioxide. Another expedient resorted to was to boil the solution to remove the dissolved air and to cool to room temperature

before the addition of acid and potassium iodide. None of these methods, apparently, were very successful.

In view of the importance of this item, experiments were performed to determine the magnitude of the liberated iodine and the influence of various factors upon the amount separating out.

Preparation of Materials—The potassium iodide was of the usual C. P. grade. This was alkaline to phenolthalein, due to the presence of a very small amount of alkali carbonate to retard decomposition. Iodate was found absent, according to the test recommended by Mellor[8], which was found to be extremely delicate. The test, in brief, was to slightly acidify a potassium iodide solution of known strength to which some starch solution had been added.

The hydrochloric acid used was the C. P. grade and was found to be free of chlorine, according to the test recommended by Krauch[9]. The specific gravity of this strong acid was determined for every bottle used. From this value, the normality was obtained by use of tables. In no case was the acid ever found to be 12 N. In some cases, the acid strength was determined by titration as well as by the gravity method.

In making up solutions of hydrochloric acid, the acid and water were measured out in ordinary graduates, since extreme accuracy was not sought.

The thiosulphate solution was neutral to litmus and was prepared by dissolving the required amount of the salt in recently boiled distilled water. The solution was filtered and showed no separation of sulphur upon standing for long periods of time. These solutions were standardized against weighed amounts of iodine, resublimed in the presence of potassium iodine and then alone. The iodine thus prepared was kept in a calcium chloride dessicator.

The following is cited as an example of the method of procedure for the 5 N acid. 190 cc. of 5.3 N HCL were poured into an Erlenmeyer flask and 10 cc. of potassium iodide solution containing the required amount of potassium iodide were added, while rotating the flask to avoid local excess. This brought the acid concentration to 5 N. The flask was allowed to stand the required length of time and then titrated with dilute thiosulphate solution to the disappearance of the iodine color. The total volume before titration was in each case 200 cc. In the experiments where smaller concentrations of acid were used, the 5.3 N acid was diluted, so that when the 10 cc. of potassium iodide solution was added, the final concentration would be the required normality. The experiments were run in duplicate and the mean appears in the table.

TABLE I.

Cons. HCL	Time mins.	Gms. KI	cc. .03N $S_2O_3^=$ sol.	Equiv. N $S_2O_3^=$ $\frac{1}{10}$ sol.	Time mins.	cc. .03N $S_2O_3^=$ sol.	Equiv. cc. N $S_2O_3^=$ $\frac{1}{10}$
2N	10	3	.14	.04 cc.	20	.21	.06
3N	10	3	.25	.08	20	.39	.12
4N	10	3	.35	.11	20	.66	.20
5N	10	3	.68	.20	20	.85	.26
2N	..	...	...	...	..	...	...
3N	..	1.5	...	...	20	.20	.06
4N	..	1.5	...	...	20	.29	.09
5N	10	1.5	.43	.13	20	.54	.16

TABLE II.

4N	..	3	...	...	20	.60	.18
5N	..	3	...	...	20	.90	.27

Table II represents the mean results of two sets of experiments carried out to determine the action of light upon the liberation of iodine. The flasks were wrapped in heavy black cloth and at the end of the allotted time were removed. The liberated iodine was determined in the same manner as the others.

In comparing the two tables, it is evident that there is little difference between the results obtained by allowing the reaction mixture to stand in the dark and in the light. All these experiments were carried out in a north room away from direct sunlight. There is no doubt that in a strong light, such as direct sunlight, the amount of iodine liberated is comparatively large. Some experiments carried out in the morning and late afternoon showed slightly larger amounts of iodine liberated in the former case. The difference was small, but quite noticeable.

From Table I, it is evident that the amount of iodine liberated depends upon the concentration of acid, potassium iodide and the time they are allowed to remain in contact, the amount liberated increasing with increase in concentration of the above substances and with the duration of time. The effect of diffused light for the conditions of the experiment is slight. Temperature, however, has a decided effect, as will be shown later.

III. DECOMPOSITION OF THIOSULPHATE BY STRONG ACIDS.

The decomposition of thiosulphate by strongly acid solutions introduces another serious error in the method. The extent of decomposition is dependent mainly upon the strength of the acid, thiosulphate solution and the rate of delivery into the acid solution.

In order to determine the magnitude of this decomposition, the following series of experiments were performed: Acid solutions of various concentrations were made so that, after the addition of iodine solution, the final concentration would be that indicated in Table III. Before the addition of the iodine solution, carbon dioxide was passed through the solution to remove air. Iodine solution containing 3 gm. KI was added and the solution allowed to stand ten minutes before the iodine was rapidly titrated with .1N thiosulphate to the disappearance of color. Similar solutions were titrated slowly, drop by drop, in order to determine whether the rate of delivery had any appreciable effect upon the decomposition. The total volume in each case was 200 cc. before titration. All titrations were run in duplicate. The burette used for these experiments was one whose delivery rate was 50 cc. in about 40 seconds. During the titration, the Erlenmeyer flasks were rotated in order to prevent, as much as possible, a local excess of thiosulphate in the solution.

TABLE III.

Conc. HCL N	cc. Iodine solution	cc. $\frac{N}{10}$ $Na_2S_2O_3$ sol. Added rapidly	cc. $\frac{N}{10}$ $Na_2S_2O_3$ sol. Added slowly	Error in cc. $\frac{N}{10}$ $Na_2S_2O_3$ sol. Rapidly	Error in cc. $\frac{N}{10}$ $Na_2S_2O_3$ sol. Slowly
0	20.00	17.53	.....	....	....
4.8	20.00	17.70	17.63	.17	.13
4.0	20.00	17.62	17.60	.09	.07
3.0	20.00	17.59	17.59	.06	.06

Blanks run under the same conditions with no iodine but with 3 gm. of potassium iodide showed a liberation of iodine equivalent to .02 cc. of thiosulphate solution.

The table shows that the decomposition is quite appreciable for the 4.8 N HCL, which is slightly under that present in the Williamson method. It is also evident that the slow rate of delivery, especially with large acid concentrations, is somewhat effective in cutting down this decomposition.

It is not customary, in quantitative work, to use a burette with a delivery rate as high as 50 cc. in 40 seconds. In order to parallel conditions obtaining in Williamson's process, another series of experiments were performed, using a burette with a delivery of 50 cc. in 90 seconds. This represents the minimum time allowable and should, therefore, represent the worst permissible condition with respect to the delivery rate in an actual analysis.

The amount of iodine liberated in an actual determination is usually equivalent to about 30 cc. of .1N thiosulphate solution. The experiments were adjusted to conform with the above condition. No carbon dioxide was used, but the iodine was titrated immediately after its addition.

To illustrate the procedure, the experiment for the 5 N hydrochloric acid is cited. To 43 cc. of 11.6 N HCL in an Erlenmeyer flask, 27 cc. of water are added. Into this with shaking are delivered by means of a pipette 30 cc. of iodine solution, containing sufficient potassium iodide to keep iodine in solution. The iodine solution is immediately titrated by means of approximately .1 N thiosluphate solution with stop cock open full to the disappearance of color. The flask was given a rotary motion to avoid local excess of thiosulphate solution. The total volume in each case before titration was 100 cc. The values appearing in Table IV represent the mean of many determinations.

TABLE IV.

Conc. HCL N	cc. Iodine solution	cc. $\frac{N}{10}$ $S_2O_3^=$ sol.	Error in cc. $\frac{N}{10}$ $S_2O_3^=$ sol.
0	30	31.49	.....
1	30	31.48	+.01
2	30	31.49	.00
3	30	31.48	+.01
4	30	31.44	+.05
5	30	31.52	—.03
6	30	31.59	—.10
8	30	32.11	—.62

Although the experiments listed in Tables III and IV were not run under similar conditions, they still serve to show that the decomposition of the thiosulphate when delivered from a rapid delivery burette is much more than when delivered from one with a slower rate.

It is worthy to note that with the exceptions of N, 2N, 3N and 4N concentrations, the amount of thiosulphate is in excess of that required when no acid is present. This brings up the interesting question, Why is more thiosulphate necessary to reduce the iodine? If the thiosulphate is decomposed into SO_2 and S, then the value should be smaller than that obtained for the iodine solution containing no acid, since SO_2 reduces 2 atoms of iodine while thiosulphate reduces one. This is apparently so in the case of the 4 N acid. The high results in the other cases may be explained either by the loss of SO_2 as a gas or by the reaction proposed by Volhard [17, 18]: $SO_2 + 4HI = S + 2H_2O + 2I_2$. In none of these experiments was any separation of sulphur observed. Gooch[2] is inclined to believe that the reducing action of SO_2 is dependent

upon the strength of acid and is slower and less complete the greater the acid concentration.

It is apparent, then, that the error in this case is a resultant one, due to the decomposition of thiosulphate and the partial reduction of iodine to iodide ion by means of the sulphur dioxide resulting from the decomposition. The exact compensation of these two reactions is largely a matter of chance, and, in titrations, where high acid concentrations are present, the primary action, that is, the decomposition of thiosulphate into sulphur and sulphur dioxide, predominates.

We now have sufficient data to determine at least approximately the errors introduced into the method from these two sources, namely, the decomposition of thiosulphate and the liberation of iodine due to the action of air.

If the time before titration is 10 minutes, as recommended by Rosenthaler[3], then from Table I, for 3 gm. of KI and 5 N acid, the excess liberation of iodine is equivalent to .20 cc. of .1 N thiosulphate solution. The decomposition of thiosulphate for the above conditions is given in Table IV and amounts to .03 cc. .1 N thiosulphate solution. The total error is then approximately .23 cc., which is equivalent, in round numbers, to .0021 gms. of KH_2AsO_4. This combined error alone, assuming .200 gms. of the acid arsenate taken originally, amounts to ten parts in a thousand. In some cases where a much longer time is recommended, the error, of course, is greater.

Theory of Reaction.

If a solution of potassium iodide is added to a solution of arsenic acid, iodine is liberated as a result of the oxidation of iodide ion while the arsenate is reduced to trivalent arsenic. The reaction may be expressed ionically as follows: $AsO_4^{\equiv} + 2H^+ + 2I^- \rightleftarrows AsO_3^{\equiv} + H_2O + I_2$. This reaction is a reversible one and may be made to go quantitatively in either direction, depending upon the concentration of the reacting materials. The reverse action, iodine plus arsenite giving arsenate plus iodide ion in the presence of a small concentration of hydrogen ion, has been a standard method for the determination of trivalent arsenic. Washburn[10] has fixed conditions from theoretical considerations, which makes the method one of the most accurate we possess. The forward action, arsenate to arsenite in the presence of much strong acid and iodide ion, is the basis of Williamson's method for pentivalent arsenic.

This action may be made more or less complete by varying the concentrations of the reacting constituents. The equilibrium may be displaced from left to right by increasing the concentration of the substances

on the left and by decreasing the concentration of those on the right. Since the arsenate is to be determined, it is apparent that we cannot increase its concentration. As for the iodine, by virtue of its being a reaction product between arsenate and iodide ion, serves as an indication of the amount of arsenic present in the pentavalent condition and cannot be removed except during the actual titration by means of thiosulphate. The remaining substances that may possibly be varied in order to bring about complete action to the right are the acid, iodide, and trivalent arsenic.

A high concentration of hydrogen ion and iodide ion favors the forward action but, in view of the fact that the higher the concentration of hydrogen ion and iodide ion, the greater the liberation of iodine due to the presence of dissolved oxygen, some attempts were made to reduce the concentration of trivalent arsenic.

If the trivalent arsenic could be tied up in a complex ion and thus remove it from the reaction, it might be possible to use a smaller hydrogen ion and iodide ion concentration, thus cutting down the value for the excess liberation of iodine and also reducing the extent of the decomposition of thiosulphate by strong acids. Unfortunately, trivalent arsenic does not seem to enter very readily into complex ion formation, and, after one attempt, using flouride ion, this method was abandoned.

Certain organic compounds, however, react with trivalent arsenic and it was thought possible to obtain one which might combine readily with it under the conditions for the determination. The compounds used must, of course, be soluble in water and not react with the liberated iodine. This condition eliminates a great many substances. The reaction between trivalent arsenic and organic compounds takes place very slowly and in the presence of strong alkali. The necessity of strong acid in the method renders the reaction useless for our purpose. One organic compound, however, was tried on the strength of the statement made by Quick and Adams[11] that ethylene chlorhydrin reacts rapidly with sodium arsenite and that in ten minutes eighty per cent. of the arsenite is converted. Although alkaline solution is specified, it was thought that in a slightly acid solution, the reaction might proceed to a certain extent. It was found, however, that in a tenth normal hydrochloric acid solution no reaction took place between the arsenite and ethylene chlorhydrin at the end of one half hour.

Having failed in the attempt to remove the trivalent arsenic by tying it up with organic and inorganic substances, the two remaining substances upon which the completeness of reaction depends are the acid concentration and the iodide concentration.

The iodide concentration will be limited by several factors. First, sufficient potassium iodide must be present at the end of the action so

that no iodine separates out in solid form. This consideration sets the minimum value for the potassium iodide concentration. It has been shown that the amount of iodine liberated by the presence of oxygen in the solution increases with increase in potassium iodide concentration. So, although the action is favored by a high concentration of potassium iodide, its concentration must be limited with the intention of keeping this excess iodine to a minimum value. An excess of potassium iodide has also a very marked effect in favorably decreasing the reverse action.

IV. THE CONCENTRATION OF ACID TO SECURE COMPLETE OR NEARLY COMPLETE ACTION.

The proper acid concentration for this action has always been in doubt. Williamson's procedure calls for acid of specific gravity 1.16, which, when added to the solution, gives a concentration of about 5 N before titration with thiosulphate. Rosenthaler recommended an acidity about 3.5 N. Kolthoff set the minimum value at 4 N. Later, Rosenthaler[6] admitted that 3.5 N is too low and advises the use of a stronger acid solution, which is approximately the same as recommended by Williamson. In this work, we have been able to fix the acid concentration as 6 N by a method independent of the usual titration of the liberated iodine by thiosulphate.

The titration with thiosulphate does not indicate that the reaction is complete at the end of a certain period of time, because during the titration, the removal of iodine favors the completion of the action. Further, thiosulphate converts iodine to iodide ion, which also favors the displacement of equilibrium in the right direction. Hence, this method of attack gives no information as to the extent of the completeness of the reaction in the acid recommended.

The method employed by us to fix the acid concentration makes use of the principle of electrometric titrations.

It is often assumed that the addition of acid is simply to liberate hydriodic acid from the potassium iodide. It may be easily shown that the hydrochloric acid is added not solely to liberate hydriodic acid but to bring about the conversion of arsenic acid to give probably pentavalent arsenic ion.[19] This statement may be tested by connecting two beakers by means of a salt bridge and completing the circuit through two platinum electrodes and a millivoltmeter. One beaker contains sodium arsenate solution with one platinum electrode and the other beaker potassium iodide solution and the second platinum electrode. The addition of HCL to the potassium iodide solution is registered by a very slight move-

ment of the millivoltmeter needle, while the addition of HCL to the arsenate solution gives a decided displacement to the needle, showing that the addition of HCL to the arsenate solution increases the oxidizing power of arsenic acid rather than the reducing power of hydriodic acid.

The arsenic acid, although quite a strong acid, may be looked upon as amphoteric, showing basic properties to a slight extent as well as its usual acid properties. An increase in hydrogen ion concentration should favor the basic ionization, resulting in a greater increase of pentavalent arsenic. The action may be formulated as follows:

$$H_3AsO_4 + H_2O \rightleftarrows As(OH)_5 \rightleftarrows As^{v} + 5OH^{-} \left.\begin{matrix}\\ H^{+}\end{matrix}\right\} \rightleftarrows H_2O.$$

The pentavalent arsenic may be looked upon as the oxidizing agent liberating free iodine, itself being reduced to the trivalent condition. $As^{v} + 2I^{-} \rightarrow As^{'''} + I_2$. This view is in keeping with the fact that arsenic acid is much stronger in acid solution as an oxidizing agent than it is in neutral or weakly acid solution. Since the hydrogen ion promotes the oxidizing action of the arsenic acid and not the reducing action of hydriodic acid, it is evident that its concentration plays a very important part in the reaction arsenate to arsenite.

The Electrometric Titration of Arsenic Acid by Potassium Iodide.

The principle underlying all electrometric titrations is a general one and is not merely applicable to a few special reactions.

In the titration of arsenic acid with potassium iodide solution, the first additions of potassium iodide solution result in a slight change of E. M. F. If conditions are favorable, the iodide ion is practically entirely oxidized. A point is soon reached, however, where the concentration of arsenate ion has been reduced to an extremely small value. The concentration of iodide ion at this point is also small. One drop of iodide solution at this point produces a very large percentage change in both the concentration of iodide ion and arsenate ion, increasing it in the former case and decreasing it in the latter. This point is indicated by a very large change in potential with a small addition of iodide solution and represents the end point of the reaction.

Plotting the E. M. F. of the system Hg-HgCl Sat KCl———Arsenate Iodide-Pt. against volume of reagent added should give, if the reaction is complete, curves with definite points of inflection.

The E. M. F. measurements were made by means of a Leeds and Northrup potentiometer and a D'Arsonval galvanometer. A Weston cell was used as a primary standard of reference. A saturated calomel cell

described by Fales and Mudge[12] was used as a half cell. The other electrodes used were platinum wire, platinum foil and gold foil. These were sealed into glass tubes. The platinum wire was .4 mm. in diameter and 6 mm. long. The platinum foil and gold foil were 2cm. long and 1 cm. wide. The electrodes were used bright.

Procedure—Into the reaction bottle was placed a certain weight of arsenic acid solution. To this was added sufficient concentrated hydrochloric acid of known normality to bring the solution to the required concentration. Into this solution dipped the long arm of the calomel cell, the three electrodes and a stirrer, which was motor driven. No attempt was made to exclude air. The absolute values for the potentials were not sought; it was simply desired to determine which acid concentration gave points of inflection in the curves obtained by titrating the arsenic acid by means of approximately .1 N potassium iodide solution. The potassium iodide was run into the mixture in small increments and the E. M. F. taken when equilibrium had been reached. In the following tables, only the equilibrium values are given. The arsenic acid used in these experiments was made by oxidizing pure arsenious oxide by means of nitric acid, and subsequently removing the nitric acid by evaporation with water. The arsenic acid was crystallized out and showed no test for nitrate, using the diphenylamine reagent. The solution used in the following experiment was made from these crystals.

N HCL

17.9 cc. 11.2 N HCL
5 cc. H_3AsO_4 Sol. equiv. .181 gms. As_2O_5
182 cc. H_2O
Total volume before titration—205 cc.
Acid strength before titration with KI—1N

Time	cc. $\frac{N}{10}$ KI	E platinum wire as electrode
3:25	5	.3853 V.
4:13	15	.3704
5:03	25	.3629
5:35	37	.3549
6:20	50	.3500

2 N HCL

36 cc. 11.2 N HCL.
5 cc. H_3AsO_4 sol. equiv. .195 gms. As_2O_5
159 cc. H_2O
Total volume before titration—200 cc.
Acid strength before titration—2 N.

Time	cc. $\frac{N}{10}$ KI	E volts Pt. foil	E Volts Pt. wire
1:35	0.00	.1906	.3341
2:27	9.00	.3908	.3918
3:15	17.00	.3806	.3813
4:08	27.00	.3725	.3725
4:28	32.00	.3686	.3687
5:10	34.03	.3677	.3678
5:28	35.00	.3664	.3670
5:35	36.00	.3661	.3658
6:27	40.00	.3631	.3636
6:50	50.00	.3590	.3590

4 N HCL

72 cc. 11.2 N HCL
5 cc. H_3AsO_4 sol. equiv. .191 gms. As_2O_5
124 cc. H_2O
Total volume before titration—201 cc.
Acid strength before titration—4 N.

Time	cc. $\frac{N}{10}$ KI	E volts Pt. foil	E Volts Pt. wire
1:40	0.00	.3448	.4925
2:52	9.00	.4128	.4145
3:28	17.00	.3996	.4002
4:05	27.00	.3869	.3875
4:35	32.00	.3823	.3825
4:50	33.00	.3813	.3815
5:00	34.02	.3803	.3804
5:15	36.00	.3784	.3786
5:35	42.01	.3737	.3739
6:16	50.00	.3687	.3687

6 N HCL

200 cc. 6.2 N HCL
5 cc. H_3AsO_4 sol. equiv. .191 gms. As_2O_5
Total volume before titration—205 cc .
Acid strength before titration—6 N

Time	cc.—$\frac{N}{10}$ KI	E volts, gold foil	E volts, Pt. foil	E volts, Pt. wire
11:10	0.00	.4946	.4729	.5150
12:15	5.20	.4974	.4963	.4987
12:50	10.00	.4890	.4881	.4896
1:17	15.18	.4764	.4750	.4774
2:00	28.50	.4337	.4317	.4331
2:35	30.00	.4274	.4259	.4275
2:59	31.00	.4232	.4214	.4227
3:22	32.00	.4179	.4164	.4169
3:45	32.52	.4146	.4132	.4140
4:10	33.00	.4110	.4099	.4106
4:30	33.20	.4097	.4085	.4093
5:00	33.53	.4073	.4050	.4068
5:25	34.01	.4029	.4010	.4023
6:08	37.00	.3775	.3768	.3771
6:25	41.00	.3585	.3578	.3578
6:30	46.00	.3478	.3470	.3479
	50.00			.3431

8 N HCL

143 cc. 11.2 N HCL.
5 cc. H_3AsO_4 sol. equiv. .190 gms. As_2O_5
52 cc. H_2O
Total volume before titration—200 cc.
Acid strength before titration—8 N

Time	cc. $\frac{N}{10}$ KI	E volts Pt. foil	E Volts Pt. wire
1:55	0.00	.2207	.4655
3:06	9.00	.4992	.5034
4:10	17.00	.4950	.4967
5:10	27.05	.4691	.4694
6:30	32.02	.4447	.4494
7:05	32.50	.4417	.4462
7:40	33.03	.4345	.4390
8:20	33.50	.4249	.4291
8:55	34.00	.4117	.4146
9:15	35.00	.3875	.3886
9:25	36.10	.3730	.3733
9:35	41.00	.3463	.3461
9:40	46.00	.3360	.3360
9:50	50.00	.3300	.3300

11 N HCL

200 cc. 11.2 N HCL
5 cc. H_3AsO_4 sol. equiv. to .189 gms. As_2O_3
Total volume before titration—205 cc.
Acid strength before titration—10.9 N.

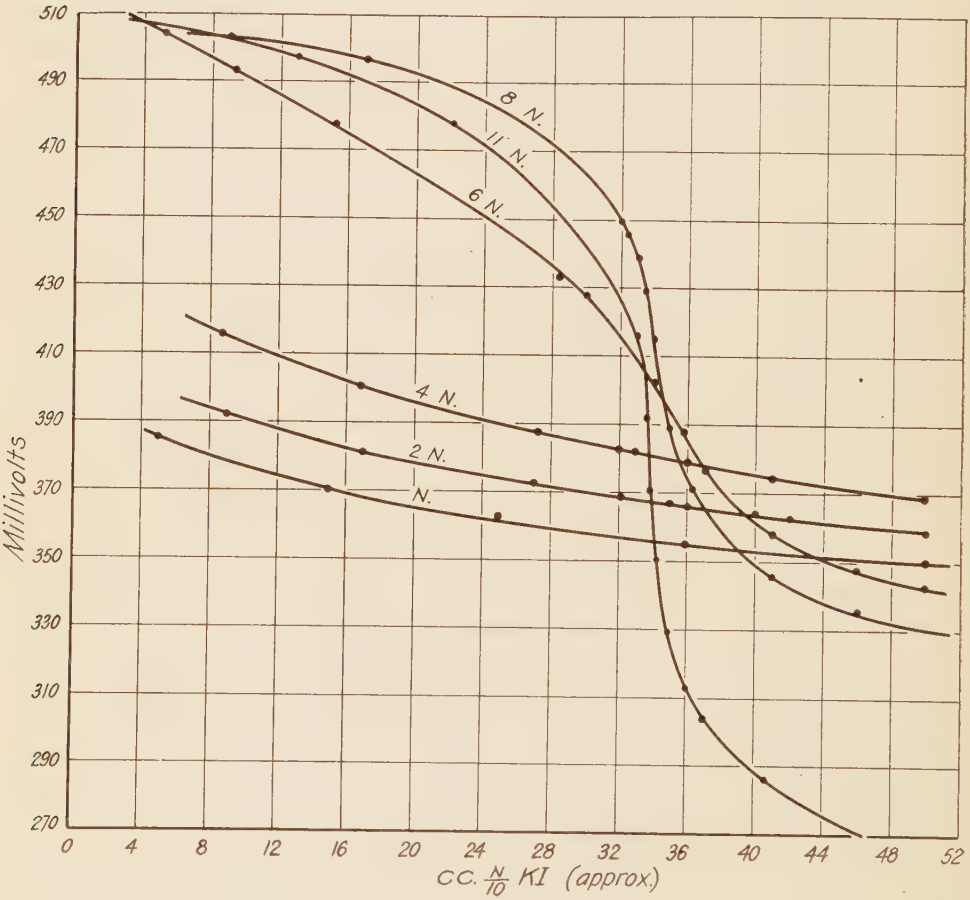
Time	cc. $\frac{N}{10}$ KI	E volts Pt. foil	E Volts Pt. wire
12:55	0.00	.4067	.5099
2:13	6.00	.5190	.5318
3:05	13.00	.4959	.4974
3:45	22.10	.4776	.4775
4:10	33.00	.4176	.4162
4:50	33.30	.4071	.4082
5:05	33.60	.3911	.3924
5:20	33.80	.3772	.3792
5:30	33.90	.3690	.3711
5:45	34.40	.3457	.3466
6:10	35.00	.3280	.3283
6:20	36.00	.3125	.3127
6:25	36.50	.3075	.3078
6:30	37.00	.3036	.3036
6:35	42.00	.2814	.2814
7:10	50.00	.2686	.2686

Plotting these values for the different acidities, we obtain the curves in Figure I. The curves show at a glance that the greater the acid concentration, the sharper is the inflection. The curves representing the titrations in N, 2 N, 4 N HCL, show no points of inflection whatever, which indicates that at no time during the titration is the action complete. In direct contrast are the curves due to the titrations in 6 N, 8 N and 11 N, HCL. The 6 N curve shows an inflecion which, although not very sharp, is very pronounced and indicates that the reaction in 6 N HCL is complete, or very nearly so. There is no comparison between the 6 N and the 4 N curves with respect to the completeness of reaction. The 8 N curve shows a sharp well-defined inflection far better than that of the 6 N curve, and would indicate complete action under the conditions of the experiment. The 11 N curve needs no comment except that, under practical conditions of analysis, it cannot be realized.

Although the conditions under which these experiments were run are not the same as those met in an actual analysis, still, the curves show, relatively, at least, that the 6 N HCL is better for the reaction than the 4 N acid, and that the 8 N is better than the 6 N acid. The 8 N acid would appear to be the best concentration in which to carry out the

action. There are, however, other considerations which enter into the selection of the proper acid concentration. It will be recalled that the amount of iodine liberated from potassium iodide due to dissolved oxygen increases with increase in acid concentration. Furthermore, the decomposition of thiosulphate is greater with the stronger acid.

The inflection shown by the 6 N acid curve, while not as well pro-



nounced as the 8 N curve, shows comparatively a fairly sharp inflection which indicates practically complete action. In view of the fact that this reaction is reversible, the equilibrium may be easily shifted by removing one of the products of the reaction. During the titration with thiosulphate, iodine is removed and, consequently, the equilibrium is displaced. So that, while it is desirable to have the reaction complete

before titrating, it is not necessary that it should be so. It should, however, be as nearly complete as possible in order that, while titrating with thiosulphate, it may be brought quickly to completion.

In view of these considerations, the 6 N acid concentration is recommended for the reaction.

This method of electrometrically titrating pentavalent arsenic may be made to give quantitative results if a few precautions are observed. It is not necessary to wait for equilibrium to set in between each addition of KI before reading the E. M. F. because the end point is given by the inflection in the curve obtained by plotting voltage against volume of reagent added, and the inflections will coincide regardless of whether the readings are taken within a few minutes after the addition of potassium iodide or after equilibrium is attained. The curve is simply shifted up or down but the point of inflection remains stationary.

It may be possible to dispense with the trouble of plotting the E. M. F. volume curve by using the rapid simplified apparatus proposed by Kelly[13] and co-workers or by Roberts[14].

The advantage of the electrometric titration of arsenate over that of the thiosulphate titration is that the arsenate may be determined in the presence of colored substances without their separation.

V. THE REVERSE ACTION.

Having now decided upon the proper acid concentration, and having determined the extent of decomposition of thiosulphate by strong acid, it remains to determine the conditions to prevent the reverse action which it is claimed sets in during the titration. Although this fear has been expressed by many who worked with the method, no one apparently has attempted to determine the extent of the reverse action upon dilution.

Roebuck [15], in attempting to determine the equilibrium constant for this reaction, has shown for the conditions of his experiments, which are not exactly the same as exist in an actual determination, that the reverse action is greatly hindered by the presence of much acid and potassium iodide. The rate of the reverse action is, according to him, directly proportional to the concentration of triiodide ion, to the concentration of trivalent arsenic, inversely as the square of the iodide ion concentration and inversely as the concentration of acid when present in greater concentration than .2 N acid.

In order to determine the extent of the reverse action in acid solu-

tions stronger than .2 N and under conditions similar to those met with in an actual analysis, the following set of experiments was performed:

To arsenite solutions of various concentrations made neutral to phenolthalein, sufficient water and dilute acid was added, so that, after the addition of the theoretical amount of iodine solution necessary to react with the arsenate, the acid concentration would be the required normality. For example, the following experiment is cited: 25 cc. of neutralized arsenite solution are pipetted into an Erlenmeyer flask. To this is added 87 cc. of water containing 2.5 gm. of potassium iodide. 62 cc. of 8 N HCL are now added, while rotating the flask. Finally, 25 cc. of iodine solution exactly equivalent to the above amount of arsenate are added from a pipette. The 25 cc. of iodine solution contains .5 gm. of KI, so that the total amount of KI present is 3 gm. The total volume is 200 cc. and the final acid concentration is 2.5 N. The solutions were allowed to stand 5 minutes and were then titrated rapidly with thiosulphate. The burette used had a rapid delivery rate of 50 cc. in 40 seconds. This burette was employed in order to offset as much as possible the displacement of equilibrium due to the removal of the iodine. In this way, it was possible to detect the slight reversibility indicated in the following table.

In view of the fact that during the titration the equilibrium is being constantly displaced, the results indicated must be looked upon as only relative and in no sense strictly quantitative. They serve the purpose, however, is showing that during an actual titration of iodine with a burette of normal delivery, the danger of the reverse action introducing a serious error is unfounded, since, at the end of the titration, in Williamson's process, the acid concentration, assuming 40 to 50 cc. of thiosulphate used, is between 2.5 to 3 N.

In experiments 1 to 5 inclusive, the 50 cc. iodine solution were equivalent to 37.2 cc. thiosulphate. In experiments 6, 9 and 10, the 25 cc. iodine solution were equivalent to 21.0 cc. thiosulphate, and in experiments 7, 8, 11 and 12, the iodine solution was equivalent to 17.60 cc. of diluted thiosulphate solution. All the experiments were run in duplicate.

TABLE V.

Exp. No.	Conc. HCL	cc. of arsenite sol.	cc. Iodine sol.	Total KI gms.	Total Vol. cc.	Time standing, mins.	Approx. norm. of acid at end of titr.	Amt. I_2 sol. used up cc.	% I_2 sol. used in reverse action
1.	.1 N	25 cc. .271 g. As_2O_3	50	3	200	5	....	14.3	28.6
						10	....	22.09	44.3
						15	....	26.18	52.4
2.	2 N	Same as above	50	3	200	5	1.7	.5	1.
3.	N	Same as above	50	3	200	5	.9	2.2	4.3
4.	N	Same as above	50	1	200	5	.9	8.9	17.6
5.	3 N	Same as above	50	3	200	5	2.5	None Slight excess found	No reverse reaction indicated
6.	2 N	25 cc. .153 g. As_2O_3	25	3	200	5	1.8	.05	.2
7.	2 N	25 cc. .075 g As_2O_3	25	3	200	5	1.8	Slight excess found	No reverse reaction indicated
8.	2 N	Same as above	25	1.5	200	5	1.8	.03	.12
9.	2.5 N	25 cc. .153 g. As_2O_3	25	3	200	5	2.2	Slight excess found	No reverse reaction indicated
10.	2.5 N	Same as above	25	1.5	200	5	2.2	.10	.40
11.	2.5 N	25 cc. .075 g As_2O_3	25	3	400	5	2.4	None	No reverse reaction indicated
12.	2.5 N	Same as above	25	1.5	400	5	2.4	.16	.63

In all the experiments, the titration with thiosulphate should show a slight excess of iodine over that taken if no reverse action had taken place, due to the iodine liberated by the HCL. The experiments in which an excess of iodine was found are indicated.

The table shows in a striking manner the effect of varying the concentration of the various reagents. Experiments 3 and 4 show that the concentration of KI has a marked effect upon the speed of the reverse action. In all the experiments where KI used is below 3 gms., reverse action is indicated. Experiments 6 and 7 show the effect of changing the concentration of As_2O_3. Experiments 7 and 8 again show the influence of the concentration of KI.

The conditions for no indicated reverse action are apparently that the acid concentration after titration be not less than 2.2 N and that 3 gms. of KI remain after the reaction, the volume being not greater than 250 cc. after titration.

The conditions under which the above experiments were carried out do not exactly conform to those for an actual analysis, first, because 5 minutes are rarely taken from the beginning to the end of the titration; second, the burette delivering the thiosulphate is one whose delivery rate is much smaller than used in these experiments.

Fortunately, the concentration of HCL which limits the reverse action to a minimum is that where the decomposition of thiosulphate is practically nil. It is, therefore, proposed to carry out the reaction in 6 N HCL, then diluting to 3 N and titrating with thiosulphate.

In order to settle definitely the question of reverse action for the conditions under which the actual determinations are to be run, the following series of experiments were performed: An iodine solution, 50 cc. of which contained 1 gm. of KI, was made exactly equivalent by titration to 25 cc. of an arsenite solution containing .231 gms. of As_2O_3. 25 cc. of this arsenite resolution was transferred to an Erlenmeyer flask and made neutral by a few drops of concentrated HCL. 37 cc. of water and 42 cc. of 11.0 N HCL were added to this solution, and it was allowed to come to room temperature before adding the equivalent 50 cc. of iodine solution. One minute elapsed from the beginning of the addition of iodine solution by means of a pipette to the beginning of the titration with thiosulphate. During the rapid titration with thiosulphate, the flask was constantly rotated until the last few drops discharged the iodine color. A blank was made titrating the same amount of iodine solution under the same conditions as above, the acid added and final volume being the same. The acid concentration, before titration with thiosulphate, is 3 N. At the end of the titration, the final concentration is approximately 2.3 N. These conditions are the same as those present in the adopted procedure. All determinations were in duplicate. The values in the following table represent the mean of two closely agreeing determinations.

TABLE VI.

	Conc. HCL	Arsenite sol.	cc. I_2 sol. necessary to react.	Total gms. KI.	cc. S_2O_3= to discharge color.	Difference in cc. S_2O_3=
	3 N	None	50	1	48.99	
1.	3 N	25 cc. .231 g. As_2O_3	50	1	48.67	.32 defic.
	3 N	None	50	2	48.71	
2.	3 N	25 cc. .231 g. As_2O_3	50	2	48.73	.02 excess
	3 N	None	50	2.3	48.63	
3.	3 N	25 cc. .231 g. As_2O_3	50	2.3	48.67	.04 excess

Experiment 1 shows that in an actual determination with large amounts of trivalent arsenic and 1 gm. of KI present after the reaction, there is some reverse action after dilution to 3 N acid before rapid titration with thiosulphate. Experiments 2 and 3 indicate that no reverse action is detected when 2 gms. or over of KI are present before the titration with thiosulphate. The burette used in these experiments had a delivery rate of 50 cc. in 90 seconds.

From the above table, it becomes evident that before the titration with thiosulphate, the reaction mixture should contain at least 2 gms. of KI when the maximum amount of arsenic is present with smaller amounts 1.5 gms. potassium iodide may be present. The final concentration of hydrochloric acid after titration should be at least 2.3 N.

It now remains to determine the magnitude of the error introduced by the liberation of iodine from potassium iodide in acid solution for the conditions adopted for the final procedure. The time recommended in the literature for allowing the reaction mixture to stand before titration varies from one minute to 30 minutes. It is obvious that the longer the time the greater will be the excess iodine liberated by the acid solution of potassium iodide. It is generally conceded that the reaction is complete in a period of 5 minutes, or, if not complete, equilibrium has set in within that time.

The following experiments were run, using 3 gms. of potassium iodide and allowing the acid solution to stand 5 minutes before diluting to 3 N and titrating with dilute thiosulphate. As an example of the procedure employed, the 6 N experiment is cited. To 36 cc. of H_2O in a 500 cc. Erlenmeyer flask 54 cc. of 11.1 N HCL are added. The solution was given a whirling motion and 10 cc. of potassium iodide solution (3 gms.) were added. It was allowed to stand 5 minutes and then 100 cc. of water added, thus bringing the concentration of acid to 3 N. The liberated iodine was titrated at once with thiosulphate .0515N. The values obtained are as follows:

TABLE VII.

Acid conc. HCL	Gms. KI	Time standing mins.	cc. $.515\frac{N}{10}$ $S_2O_3=$	Equiv. $\frac{N}{10}$ $S_2O_3=$
3 N	3	5	.09	.05
4 N	3	5	.17	.09
6 N	3	5	.24	.12
8 N	3	5	.32	.16

The 6 N acid shows a liberation of iodine equivalent to .12 cc. .1 N thiosulphate. This alone represents an error of .0011 gms. of KH_2AsO_4. This high value is due in a large measure to the heat developed upon the addition of concentrated acid to the water. The rise in temperature amounts to 10 or 12 degrees C. In order to reduce this value, the acid mixture was cooled to approximately 0^0 over ice, then removed and potassium iodide solution added. The mixture was allowed to stand on the desk 5 minutes before dilution and titration. The results are as follows:

TABLE VIII.

Acid conc. HCL	Gms. KI	Time standing mins.	cc. $S_2O_3=$ .044 N	Equiv. $\frac{N}{10}$ $S_2O_3=$
6 N	3	5	.13	.06
6 N	3	10	.30	.13
6 N	2	5	.09	.04
6 N	2	10	.19	.08
8 N	3	5	.29	.13
8 N	3	10	.60	.26
8 N	2	5	.24	.11
8 N	2	10	.51	.22

These results show that cooling before the addition of KI solution cuts down the blank in the case of the 6 N acid from .12 cc. to .06 cc.

In order to try out these conditions, potassium dihydrogen arsenate was selected because it contains no water of crystallization and is easily prepared and purified. For this work, the C. P. grade was recrystallized twice. As a check upon its constitution, the potassium and arsenic were determined upon a sample of the salt dried to constant weight. The arsenic found by the method of Gooch and Browning[16] was 54.87% calculated as As_2O_3. This value represents the mean of four closely agreeing determinations. The theoretical value is 54.96%. The potassium found was 21.73% as against the theoreical value of 21.72%. The precipitation as potassium chlorplatinate was employed with subsequent reduction to metallic platinum by powdered magnesium. The platinum was filtered off and ignited. The residue was treated with hydrofluoric acid to remove silica, and weighed after ignition.

On the basis of these determinations, the salt was considered pure and used throughout the following experiments.

With the preceding work as a basis, the following procedure is recommended: To 25 cc. of the solution at room temperature containing arsenic in the arsenate form is added sufficient concentrated hydrochloric acid of known normality so that after the addition of 2 gms. of KI in 10 cc., the acid concentration will be approximately 6 N. Immediately after the addition of the acid, the 10 cc. of KI solution (2 gms. KI) are added and the reaction mixture allowed to stand about one-half minute. The temperature of the solution will be between 30° to 35° C. due to the heat developed by the addition of concentrated HCl to 25 cc. of arsenate solution. At the end of the allotted time, the solution is diluted to 3 N acid and the iodine rapidly titrated at once to the disappearance of color.

To test the above procedure, the following experiments were performed: The KH_2AsO_4 was weighed out into 500 cc. Erlenmeyer flasks and dissolved in 25 cc. H_2O. Sufficient concentrated HCl of known normality was added so that after the addition of 2 gms. of KI in 10 cc. the acid concentration was about 6 N. The determinations were completed according to the recommended procedure. The results appear in Table A.

TABLE A.

KH_2AsO_4		Error			
Taken	Found	Gms.	Ppts. per M.	cc. S_2O_3=	$\frac{N}{10}$
.4495	.4495	.0000	0.0	48.95	1.0200
.4402	.4388	+.0014	3.2	47.77	1.0202
.4290	.4284	+.0006	1.4	46.65	1.0200
.4280	.4271	+.0009	2.1	46.49	1.0202
.4237	.4217	+.0020	4.6	45.91	1.0202
.3966	.3954	+.0012	3.0	43.05	1.0202
.3715	.3705	+.0010	2.8	40.34	1.0200
.3603	.3600	+.0003	.9	39.20	1.0200
.3592	.3591	+.0001	.3	39.10	1.0200
.3580	.3581	—.0001	.3	38.98	1.0202
.3528	.3526	+.0002	.6	38.39	1.0202
.3457	.3454	+.0003	.9	37.60	1.0202
.3414	.3415	—.0001	.3	37.18	1.0202
.3395	.3392	+.0003	.9	36.93	1.0202
.3320	.3320	.0000	.0	36.14	1.0202
.3197	.3197	.0000	.0	34.80	1.0202
.3015	.3015	.0000	.0	32.82	1.0202
.2969	.2967	+.0002	.7	32.30	1.0202
.2901	.2903	—.0002	.7	31.60	1.0202
.2759	.2758	+.0001	.4	30.03	1.0200
.2710	.2713	—.0003	1.1	29.54	1.0202
.2606	.2607	—.0001	.4	28.38	1.0202
.2565	.2565	.0000	.0	27.98	1.0202
.1895	.1897	—.0002	1.0	20.65	1.0202
.1199	.1201	—.0002	2.0	13.08	1.0202
.1159	.1162	—.0003	2.5	12.65	1.0202
.1022	.1028	—.0006	4.0	10.69	1.0202

From the above table, it is evident that the method gives good results over a wide range. The error becomes greater with decrease in weight of sample, as is to be expected. The comparatively large errors in the cases where large amounts of KH_2AsO_4 were taken is due to slight reverse action, as will be shown later.

The error due to excess liberation of iodine should give values in excess of the amounts taken if the reaction were in all cases complete.

The volume for the experiments in Table A was 150 cc. before titration. Assuming 50 cc. of thiosulphate added to discharge the color of the liberated iodine, the final acid concentration at the end of the titration would be approximately 2.3 N. In the reaction, assuming arsenic present to be equivalent to .450 gms. KH_2AsO_4, the potassium iodide necessary to react is about .8 gms. If 2 gms. of KI were added initially,

then at the end of the action there remains approximately 1.2 gms. of KI. According to Table V, the final acid concentration should not be less than 2.3 N and at least 2 gms. of KI should be present before the titration. Hence, in the above experiments, we should expect some reverse action for the large amount of acid arsenate taken, since the KI present before titration is less than 2 gms. although the final acid concentration is within the specified limit.

If a slight reverse action sets in, then the addition of KI to the water used for diluting the reaction mixture should result in giving higher values than when no KI is present in the water used for dilution. In the following experiments, the maximum amount of acid arsenate was taken, 2 gms. of KI in 10 cc. were added and the water used for dilution contained 1 gm. of KI. In other respects, the experiments were carried out in the same way as the previous set.

TABLE B.

KH_2AsO_4		Error			
Taken	Found	Gms.	Ppts. per M.	cc. $S_2O_3^=$	$\frac{N}{10}$ 1.0202—
.4549	.4554	—.0005	1.1	49.58	
.4286	.4288	—.0002	.5	46.68	
.4119	.4123	—.0004	1.0	44.89	

Comparing the results in the above table with those in Table A, the effect of the addition of 1 gm. of potassium iodide to the water used for dilution is very evident. In all the above cases, the values found are high, which is to be expected. Blank determination for the above conditions is equivalent to .07 cc. .1 N thiosluphate. This bland is, strictly speaking, too high because in the above experiments approximately 1 gm. of KI is used up in the reaction. Consequently, the amount of KI present after the reaction is about 1 gm. instead of 2. Hence, the excess liberation of iodine should correspond to that given by 1 gm. of KI.

A series of blank determinations were run for the conditions existing in the above and the following experiments. Blanks are as follows:

.1 N $S_2O_3^=$ Sol.

(1) Acid and water added to give 6 N HCl, no cooling, 1 gm. KI present, stood one-half minute before dilution and titration. Iodine liberated equivalent to..... .04 cc.

	.1 N $S_2O_3^=$ Sol.
(2) Same as above, except 2 gms. KI present. Iodine liberated equivalent to	.07 cc.
(3) Same as above, except water for dilution contained 1 gm. KI. Iodine liberated equivalent to	.07 cc.
(4) Same as Experiment 1, except 3 gms. KI added. Iodine liberated equivalent to	.09 cc.
(5) Same as (4), except acid mixture allowed to come to room temperature before the addition of 3 gms. KI. Iodine liberated equivalent to	.07 cc.
(6) Same as (2), except acid solution allowed to come to room temperature before the addition of 2 gms. KI. Iodine liberated equivalent to	.05 cc.

The thiosulphate used in the above titrations was .05 N. The values obtained were converted to decinormal readings.

In the experiments listed in Table A, the excess liberation of iodine should be equivalent to about .04 cc. .1 N $S_2O_3^=$ solution. The error introduced from this source is, therefore, equivalent to about .0002 gms. KH_2AsO_4. This represents the maximum excess acid arsenate which should be indicated in the experiments listed in Tables A and B. It is evident from the above that this error will show up much more in cases where small amounts of acid arsenate are taken than where large amounts are employed.

The reaction at room temperature and with high acid concentrations is in all probability a rapid one. Many reactions, especially the oxidation-reduction type, take place in a very short time under the proper conditions and it is this short time reaction which enables one to electrometrically titrate without the necessity of plotting the E. M. F.-volume curve in order to determine the end point.

The addition of concentrated hydrochloric acid (11-12 M.) to water in sufficient quantities to give a 6 N acid gives a rise in temperature of 10 to 12°. An increase of 10° in temperature increases the speed of this reaction twofold, according to the work of Roebuck. The increase in temperature, while increasing the speed of reaction, also increases the amount of iodine liberated due to the presence of dissolved air, but the short time allowed for the reaction to take place reduces this to a minimum, as shown above.

Further experiments were performed to see how variations in the conditions of the recommended method affected the results obtained.

In the following experiments, the conditions were the same as those in Table A, with the exception that 3 gms. of KI were added in 10 cc. of solution instead of two. The results are in Table C.

TABLE C.

KH_2AsO_4		Error			
Taken	Found	Gms.	Ppts. per M.	cc. S_2O_3=	1.0191 $\frac{N}{10}$
.4257	.4260	—.0003	.7	46.43	
.4142	.4140	+.0002	.5	45.12	
.3558	.3563	—.0005	1.4	38.83	
.3482	.3485	—.0003	.9	37.98	
.2968	.2973	—.0005	1.7	32.40	
.2568	.2576	—.0008	3.0	28.08	
.2523	.2528	—.0005	2.0	27.55	
.1634	.1641	—.0007	6.0	17.88	
.1598	.1604	—.0006	4.0	17.48	
.1418	.1422	—.0004	3.0	15.50	
.1210	.1219	—.0009	8.0	13.28	
.0985	.0992	—.0007	7.0	10.81	
.0812	.0820	—.0008	10.0	8.94	

From the above table, it is apparent that the recommended method using 2 gms. of KI gives better results over a wide variation in weights of KH_2AsO_4 taken. Here, as before, the error in ppts. per thousand is greatest with the small weights taken.

Table D shows the effect of cooling the reaction mixture to room temperature before the addition of 2 gms. of KI in 10 cc. of solution.

TABLE D.

KH_2AsO_4		Error			
Taken	Found	Gms.	Ppts. per M.	cc. S_2O_3=	.10202 N
.4292	.4288	+.0004	1.0	46.68	
.4289	.4270	+.0019	4.4	46.48	
.4275	.4262	+.0013	3.0	46.40	
.4072	.4065	+.0007	1.7	44.29	
.3894	.3879	+.0015	4.1	42.23	
.3838	.3833	+.0005	1.3	41.73	
.3763	.3757	+.0006	1.6	40.90	
.3610	.3609	+.0001	.3	39.29	
.3599	.3590	+.0009	2.5	39.08	
.3324	.3316	+.0008	2.4	36.10	
.2804	.2801	+.0003	1.0	30.49	
.2326	.2327	—.0001	.4	25.33	
.2144	.2145	—.0001	.5	23.35	
.1983	.1984	—.0001	.5	21.00	
.1041	.1046	—.0005	5.0	11.39	

In the following experiments, the acid mixture was cooled to about zero degrees over ice and ten cc. of KI solution added (3 gms. KI). The reaction mixture was allowed to stand upon the desk five minutes and rapidly titrated with thiosulphate after diluting to 3 N. The results are in the following table.

TABLE E.

KH_2AsO_4		Error			
Taken	Found	Gms.	Ppts. per M.	cc. $S_2O_3^=$	.10520N
.4601	.4602	—.0001	.2	48.58	
.4582	.4584	—.0002	.4	48.39	
.4505	.4501	+.0004	.9	47.52	
.4464	.4461	+.0003	.7	47.09	
.4075	.4076	—.0001	.3	43.03	
.3662	.3664	—.0002	.3	38.68	
.3308	.3315	—.0007	2.0	35.00	
.3302	.3303	—.0001	.3	34.87	
.3264	.3263	+.0001	.3	34.45	
.3190	.3192	—.0002	.7	33.69	.10522
.2926	.2927	—.0001	.4	30.90	.10520
.2856	.2857	—.0001	.4	30.16	
.2796	.2803	—.0007	2.5	29.58	
.2749	.2747	—.0002	.8	29.00	
.2521	.2526	—.0005	1.9	26.67	
.2494	.2499	—.0005	2.0	26.38	
.2432	.2435	—.0003	1.3	25.70	.10522
.2248	.2250	—.0002	.9	23.75	
.2207	.2208	—.0001	.5	23.30	
.1599	.1608	—.0009	6.0	16.98	.10520
.1137	.1141	—.0004	3.5	12.04	
.1102	.1106	—.0004	3.6	11.68	

Cooling the acid to about O degrees before the addition of KI, while it cuts down the magnitude of the iodine liberated due to the action of dissolved air, must also cut down the speed of reaction. According to the above experiments, this diminution in speed is not apparent under the conditions employed, for the values obtained by titration check very closely the amounts taken. The results above are equally as good as those appearing in Table A. The objection to this procedure is the bother of cooling the acid mixture over ice to about zero degrees before the addition of KI and the time interval before dilution and titration.

The following experiments were run as the previous ones, with the exception that the reaction mixture stood one-half minute before dilu-

tion and titration instead of five. The results show that the action is incomplete in this short period of time.

TABLE F.

KH_2AsO_4		Error			
Taken	Found	Gms.	Ppt. per M.	cc. $S_2O_3^=$	.10191N
.4051	.4008	+.0043	10.5	43.68	
.3587	.3533	+.0054	15.	38.50	
.3277	.3224	+.0053	16.	35.13	
.2828	.2807	+.0021	8.	30.59	

In view of the fact that the error becomes more pronounced when small amounts of arsenate are present, it is advisable that the arsenic content in the solution be equivalent to at least 25 cc. of .1 N thiosulphate.

The method was further checked by weighing out samples of pure resublimed arsenic trioxide and oxidizing them to the arsenate condition by means of concentrated permanganate solution. The trioxide was dissolved in 1 cc. of strong KOH solution and 5 cc. of permanganate solution added (20 gms. $KMnO_4$ in 400 cc. H_2O). Sufficient sulphuric acid was then added to make the solution acid. The precipitated manganese dioxide was dissolved by means of oxalic acid and the solution then made strongly acid with concentrated hydrochloric, according to the recommended procedure. It was found in all cases that the results were too high by a constant amount. The same difficulty was experienced when the oxidation was brought about by means of sodium peroxide and superoxol in alkaline solutions. In these cases the results were erratic and the permanganate oxidation was adopted since it gave consistent results. A blank determination under exactly the same conditions as the determination showed iodine liberated equivalent to .30 cc. of the thiosulphate used. A blank without any permanganate showed iodine liberated equivalent to less than .04 cc. of thiosulphate. It is apparent, then, that the high blank is due to some oxidizing impurity in the permanganate. The results in the following table have been corrected by blank determination. It is advisable to run a blank whenever oxidizing agents are used since they are rarely pure. A slight amount of ferric ion or copper liberates a very appreciable amount of iodine in a very short time, especially in a strongly acid solution. If the blank is small, the correction is unnecessary. The results appear in the following table:

TABLE G.

As_2O_3		Error			
Taken	Found	Gms.	Ppts. per M.	cc. S_2O_3=	.11237N
.2617	.2610	+.0007	3.0	46.93	
.2349	.2344	+.0005	2.0	42.16	
.2273	.2268	+.0005	2.2	40.79	
.2227	.2227	.0000	.0	40.05	
.2122	.2120	+.0002	1.0	38.13	
.2125	.2121	+.0004	2.0	38.15	
.2086	.2084	+.0002	1.0	37.48	
.1984	.1985	—.0001	.5	35.70	
.1951	.1951	.0000	.0	35.08	
.1898	.1899	—.0001	.5	34.15	
.1879	.1877	+.0002	1.1	33.75	
.1609	.1611	—.0002	1.3	28.97	
.1503	.1500	+.0003	2.0	26.98	
.1428	.1429	—.0001	.8	25.70	
.1310	.1312	—.0002	1.6	23.59	

The good agreement obtained above shows that the method will give results better than two parts in a thousand on the average. The method has much to recommend it. It is rapid and accurate and applicable to a variety of solutions where the arsenic is in the arsenate form, provided there are present no other oxidizing agents that will liberate iodine from KI.

SUMMARY

The volumetric determination of arsenic acid by titration of liberated iodine by means of thiosulphate, after reduction with potassium iodide in hydrochloric acid solution, has been studied with special reference to the conditions affecting the accuracy of the determination. It has been shown that:

1. The reduction of the arsenic acid is quantitatively complete in 6 M hydrochloric acid, according to electrometric titration curves.

2 For the effective prevention of the reverse reaction

$$AsO_4^{\equiv} + 2I^- + 2H^+ \leftarrow AsO_3^{\equiv} + H_2O + I_2$$

the hydrochloric acid concentration at the end of the titration should be at least 2.3 M.

3. For maximum amount of arsenic present, that is, an amount equivalent to 50 cc. 0.1 M thiosulphate, about 2 grams potassium iodide should be present before the titration.

4 Under the conditions recommended the decomposition of thiosulphate by hydrochloric acid and the excess liberation of iodine by dissolved oxygen are at a minimum.

5. For the final procedure adopted in this paper, the method is accurate to within two parts per thousand.

REFERENCES.

1. Williamson, Jour. Soc Dyers & Colorists, 1896, 86.
2. Gooch and Morris, Amer. Jour. Sci. 10, 151, 1900.
3. Rosenthaler, Zeit. fur Anal. Chemie 45, 596, 1906.
4. Kolthoff, Pharm. Weekblad, 38, 1919, 1322.
5. Fleury, J. Pharm. et Chimie 21, 385, 1920.
6. Rosenthaler, Zeit. fur Anal. Chemie, 61, 222.
7. Andrews, J. A. C. S. 31, 1035.
8. Mellor, A Treatise on Quantitative Inorganic Analysis, Vol 1, 287.
9. Krauch, Chemical Reagents, Scott, Greenwald & Sons, pub.
10. Washburn, J. A. C. S., Jan. 1908, Vol. 30.
11. Quick and Adams, J. A. C. S., 44, 811, 1922.
12. Fales and Mudge, J. A. C. S. 42, 2346, 1920.
13. Kelly, J. Ind. Eng. Chem., 9, 780, 1917.
14. Roberts, Amer. Chem. Journ., 41, 1359, 1919.
15. Roebuck, J. Phys. Chem. 6, 371.
16. Gooch and Browning, Amer. Jour. Sci. 40, 66, 1890.
17. Volhard, Treadwell and Hall, Quantitative Analysis, 3rd ed. 692.
18. Macaulay, J. Chem. Soc. 121, 552, 1922.
19. Stieglitz, Qualitative Analysis, Part I.
20. Barger and Field, J. Chem. Soc., 101, 1394.

VITA.

Rocco Fanelli was born in New Rochelle, New York, March 2, 1894. He was graduated from New Rochelle High School in 1914. From Columbia University he received the degrees of B. S. (1918) and A. M. (1919). From 1917 to the present time he has assisted in the Department of Chemistry of Columbia University, as well as in extension teaching. At present, he is an assistant in Quantitative Chemistry in Columbia University.